

SUPPORT FOR THE AMENDMENT

Claims 1, 3-5, and 9 have been amended.

The amendment of Claims 1, 3-5, and 9 is supported by the corresponding previously pending claims, as well as page 21, lines 3-14.

No new matter is believed to have been added by these amendments.

REMARKS

Claims 1-20 are active in the present application.

At the outset, Applicants wish to acknowledge Examiner Weiner for the helpful and courteous discussion with their undersigned Representative on August 13, 2003. The content of this discussion is reflected in the comments and amendments set forth herein. Applicants would also like to thank Examiner Weiner for the indication that the species 2,6-di-tert-butyl-4-methylpyridine and Claims 17-18 are allowable.

Favorable reconsideration and allowance of the claims is solicited.

The rejection of Claims 1-9, 11-13, and 19 under 35 U.S.C. §102(b) over the Iwakura et al is obviated by amendment.

The Examiner asserts that Iwakura et al disclose a battery comprising a cathode containing Li or Li alloy, an anode containing Mo dioxide, V pentoxide, and Li as anode active component and an electrolyte liquid. The Examiner further asserts that Iwakura et al disclose that the electrolyte contains pyridine or a pyridine derivative where R¹ to R⁵ is H or an alkyl group.

Although Iwakura et al may recite a pyridine derivative (see Claim 1), Applicants note that the pyridine derivatives disclosed in this references are distinct from the claimed pyridine derivatives. Specifically, Iwakura et al only pyridine substituted with an alkyl group having 2 or less carbon atoms, whereas the proviso of the presently claimed invention specifies that when R¹ to R⁵ are a hydrogen or an alkyl, at least one of R¹ to R⁵ is an alkyl group having 4 or more carbon atoms.

For the Examiner's convenience, Applicants note that Iwakura et al only illustrate the following pyridine derivatives:

- trimethylpyridine (the largest carbon number of the substituents is one),
- methylpyridine (the largest carbon number of the substituent is one),
- ethylpyridine (the largest carbon number of the substituent is two),
- diethylpyridine (the largest carbon number of the substituents is two),
- methylethylpyridine (the largest carbon number of the substituents is two), and
- dimethylethylpyridine (the largest carbon number of the substituents is two).

In fact, the working example Iwakura et al utilizes dimethylpyridine (the largest carbon number of the substituents is one). In contrast, in the present invention, when all of R¹ to R⁵ are a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, at least one of the alkyl groups has 4 more carbon atoms. Further, the invention of Iwakura et al is characterized by obtaining effect of improving cycle characteristics of battery. Iwakura et al neither describes nor suggests that an alkyl group having specific carbon number is selected like the present invention and that the effect of improving high-temperature characteristics of battery is obtained by the selection of the alkyl group having specific carbon number, at all.

The standard for determining anticipation requires that the reference "must teach every element of the claim" (MPEP §2131). For the reasons set forth above, Iwakura et al fail to meet this standard. Therefore, the anticipation rejection over Iwakura et al is no longer tenable.

Moreover, Applicants submit that Iwakura et al cannot even serve as the basis for a *prima facie* case of obviousness. The Federal Circuit has defined the parameters that may be considered in determining the proper use of chemical structure as the basis for obviousness rejections under 35 U.S.C. §103 in *In re Jones*, 21 USPQ2d 1941 (Fed. Cir. 1992) (**copy enclosed**). The court cited the following examples of relationships that have given rise to a *prima facie* case of obviousness:

triorthoesters and tetraorthoesters;

stereoisomers;
adjacent homologs and structural isomers; and
acid and ethyl ester (*Id.*, at 1943).

In the present case, there exists no motivation to modify the compounds disclosed by Iwakura et al to obtain the claimed pyridine compounds because Iwakura et al is silent in this regard and because the relationship between the claimed compounds and those disclosed by Iwakura et al fail to satisfy any of the above-mentioned relationships to be defined as homologs by the Federal Circuit.

In view of the foregoing, withdrawal of this ground of rejection is requested.

The rejection of Claims 1-9, 12-16, and 19 under 35 U.S.C. §102(b) over the Tsutsumi et al is obviated by amendment.

Tsutsumi et al disclose an electrolytic solution for a lithium secondary battery having an electrolyte; an organic solvent; and an additive, wherein the additive is an aromatic nitrogen-containing heterocyclic compound such as pyrazine, quinoxaline, indole, phenazine, phthalazine, pyrimidine, or a mixture thereof (Abstract).

In the compound represented by the general formula (I) as recited in claim 1 and in column 2, lines 8-28 of Tsutsumi et al, the substituents of the pyridine derivatives are limited to a lower alkyl group having 1 to 3 carbon atoms. This disclosure is distinct from that of the present invention. Further, examples of substituents other than the alkyl group in Tsutsumi et al include a halogen atom, phenyl group and hydroxyl group. However, regarding the halogen atom, Tsutsumi et al only disclose that "examples of the halogen atoms include chlorine atom and bromine atom" in column 3, line 2. In contrast, in the present invention, an example of the substituent includes fluoro group. Further, Tsutsumi et al disclose, as an example of the substituent, phenyl group, but does not illustrate any specific example. The present invention

sets for that when R¹ to R⁵ independently represent a phenyl group, two or more of R¹ to R⁵ represent phenyl groups. In other words, when a phenyl group is present in the claimed pyridine derivative, there are at least two phenyl groups.

Further, the invention of Tsutsumi et al is characterized by obtaining effect of improving cycle characteristics of battery. Tsutsumi et al neither disclose nor suggest that the effect of improving high-temperature characteristics of battery is obtained by an alkyl group having specific carbon number like the present invention, at all.

Therefore, under the standard for determining anticipation under MPEP §2131 and the obviousness test set forth in *In re Jones (supra)*, Applicants submit that the present invention is neither anticipated by nor obvious in view of Tsutsumi et al.

Withdrawal of this ground of rejection is requested.

The rejection of Claims 1-9, 12-16, 19-20 under 35 U.S.C. §102(b) over Seumori et al is obviated by amendment.

The Examiner asserts that Suemori et al disclose a battery comprising a positive electrode, a negative electrode made of a carbon-based material, and a non-aqueous electrolytic solution containing pyridine or a pyridine derivative. Applicants note that although Claim 1 of Suemori et al recites pyridine or a pyridine derivative, the compound recited in claim 2 or described in the detailed description clearly is only picoline substituted with an alkyl group having one carbon atom.

Further, Suemori et al discloses: "Examples of pyridine derivatives include alkylpyridines a hydrogen atom at an ortho, meth or para position of the pyridine moiety of which is substituted with an alkyl group having 1 to 3 carbon atoms, etc." (see paragraph [0006]). In contrast, in the present invention, when all of R¹ to R⁵ are a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, at least one of the alkyl groups has 4 more carbon

atoms. Accordingly, the pyridine derivative as described in Suemori et al is clearly different from the compound according to the present invention.

Moreover, the invention of Suemori et al is characterized by obtaining effect of improving cycle characteristics of battery. Suemori et al neither disclose nor suggest that an alkyl group having specific carbon number is selected like the present invention and that the effect of improving high-temperature characteristics of battery is obtained by the selection of the alkyl group having specific carbon number.

In view of the foregoing, under the standard for determining anticipation under MPEP §2131 and the obviousness test set forth in *In re Jones (supra)*, Applicants submit that the present invention is neither anticipated by nor obvious in view of Tsutsumi et al.

Withdrawal of this ground of rejection is requested.

The rejections of Claim 10 under 35 U.S.C. §102(b) and/or under 35 U.S.C. §103(a) over Iwakura et al, Tsutsumi et al, or Seumori et al are obviated by amendment.

Iwakura et al, Tsutsumi et al, and Seumori et al are discussed above with respect to Claim 1. As stated above, Claim 1 is neither anticipated by nor obvious in view of Iwakura et al, Tsutsumi et al, or Seumori et al. Claim 10 depends directly from Claim 1; therefore, for the same reasons set forth above for Claim 1, Claim 10 is not anticipated by or obvious in view of the disclosures of Iwakura et al, Tsutsumi et al, and Seumori et al.

Applicants request withdrawal of these grounds of rejection.

The rejection of Claims 7-8 and 10 under 35 U.S.C. §112, second paragraph, is traversed.

With respect to Claims 7 and 8, the Examiner has taken the position that the phrase "aforesaid substituents" is unclear. Applicants note that Claims 7 and 8 depend directly from

Claim 1; therefore, the artisan would readily understand that the phrase "aforesaid substituents" refers to the substituents recited in Claim 1. Namely this phrase would include the following definition for the recited substituents: R¹ to R⁵ independently represents a hydrogen atom or a substituent composed of an alkyl group having 1 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms, an alkoxy group having 1 to 4 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, a dialkylamino group having 2 to 8 carbon atoms, a 3-thienyl group, a cyano group, a fluoro group, an alkoxy carbonyl group having 1 to 6 carbon atoms, an aryl carbonyl group having 6 to 10 carbon atoms, an alkyl carbonyl group having 1 to 12 carbon atoms, a cyano alkyl group having 1 to 4 carbon atoms, an alkoxy carbonyl alkyl group having 3 to 13 carbon atoms, a pyrrol-1-ylmethyl group, a 1-pyrrolidinyl group, a 1-piperidino group, a phenyl group, a 1H-pyrrol-1-yl group, an alkoxy alkyl group having 2 to 12 carbon atoms, a dialkylamino alkyl group having 3 to 18 carbon atoms, an aryloxy group having 6 to 10 carbon atoms, an aryl alkyl group the aryl moiety of which has 6 to 10 carbon atoms and the alkyl moiety of which has 2 to 6 carbon atoms, an isothiocyanato group, a dialkylaminocarbonyl group having 2 to 8 carbon atoms, a 5-oxazole group, a trifluoromethyl group, a 1-pyrrolidine-2,5-dione group, a 1H-pyrrol-1-yl alkyl group having 1 to 6 carbon atoms, a 4,5-dihydro-oxazol-2-yl group, a 1,3,4-oxadiazol-2-yl group, a nitro group, a 1-piperidinyl group, a 1-alkylpyrrol-2-yl group having 1 to 6 carbon atoms, a 4-1,2,3-thiadiazole group, a 2-1,3,4-oxadiazole group, a morpholino group and a 1-pyrrolin-2-yl group, with the recited provisos (see Claim 1).

Regarding Claim 10, the Examiner has taken the position that the phrase "calculated according to ab initio method... the adduct between the pyridin compound and hydrofluoric acid..." is unclear. Not only does the claim provide all the context necessary to reasonably convey the scope of the claim with sufficient clarity, Applicants offer the following additional comments. Moreover, as evidence that the ab initio method would be well

appreciated by the skilled artisan, Applicants **enclose herewith** Hehre et al, "Ab Initio Molecular Orbital Theory", John Wiley & Sons. Inc. New York 1986 ISBN 0-47X-81241-2, for the Examiner's reference.

The ab initio method is a method of molecular orbital calculation that is widely used in molecular quantum mechanics and is a method of quantitatively calculating chemical phenomena by strictly solving Schrodinger partial differential equation without using the experimental value. (see page 1, line 14, Prologue) Gaussian 94 is the name of a commercially available program (maker: Gaussian Inc.) for ab initio calculations.

Generally, a wave function expressing a molecule is represented by a product of molecular orbital, and the molecular orbital is represented by a combination of functions called basis set (base set) (see page 7, line 4). The precision of calculation varies depending upon a kind of "base set" to be used, and in claim 10, 3-21G is selected as "base set".

In claim 10, energy value of a pyridine compound is obtained via working of obtaining the most stable structure of the pyridine compound using Gaussian 94 based on the ab initio method. Similarly, the energy value of hydrofluoric acid and the energy value of adduct in a state of bonding pyridine compound and hydrofluoric acid are obtained. Using such values, the energy value of adduct is subtracted from sum of (the energy value of pyridine compound) and (the energy value of hydrofluoric acid) to obtain bonding energy of pyridine compound and hydrofluoric acid.

In view of the foregoing, Applicants believe that the language of the claims are such that a person of ordinary skill in the art could interpret the metes and bound of the claims so as to understand how to avoid infringement (MPEP §2173.02). Applicants note that this rejection appears to be because the Examiner merely wants the Applicant to improve the clarity or precision of the language used. However, since the skilled artisan can readily

appreciate the meaning of the claims, Applicants submit that further amendments are unnecessary. Therefore, Applicants request withdrawal of the claim objections pursuant to MPEP §2173.02.

Acknowledgement that this ground of rejection has been withdrawn is requested.

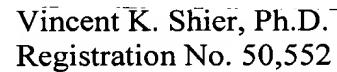
Applicants submit that the present application is now in condition for allowance. Early notification of such action is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



Norman F. Oblon
Attorney of Record
Registration No. 24,618


Vincent K. Shier, Ph.D.
Registration No. 50,552



22850

Tel.: 703-413-3000
Fax: 703-413-3220
NFO:VKS

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In re Jones (CA FC) 21 USPQ2d 1941

In re Jones

U.S. Court of Appeals Federal Circuit
21 USPQ2d 1941

Decided February 28, 1992
No. 91-1380

Headnotes

PATENTS

**1. Patentability/Validity -- Obviousness -- Relevant prior art -- Particular inventions
(§ 115.0903.03)**

Claimed novel salt of acid commonly known as "dicamba" is not so closely related in structure to substituted ammonium salts disclosed in prior patent as to be *prima facie* obvious, since claimed salt is primary amine with ether linkage, whereas diethanolamino salt disclosed in reference patent is secondary amine without ether linkage, since claimed salt is plainly acyclic or linear, whereas morpholino salt, which is only substituted ammonium salt of dicamba with ether linkage disclosed in reference patent, is cyclic in structure, and since isopropylamino salt disclosed in reference patent is primary amine, but has iso-structure quite different from that of claimed salt.

**2. Patentability/Validity -- Obviousness -- Relevant prior art -- Particular inventions
(§ 115.0903.03)**

Claimed novel salt of acid commonly known as "dicamba" cannot be held *prima facie* obvious in

view of salts disclosed in prior patent, even though claimed salt is member of genus of substituted ammonium salts broadly disclosed in reference patent, since reference discloses potentially infinite genus of "substituted ammonium salts" of dicamba, and lists several such salts, but does not specifically disclose salt claimed in application, and since claimed salt is not sufficiently similar to those disclosed in reference as to render it *prima facie* obvious.

3. Patentability/Validity -- Obviousness -- Combining references (§ 115.0905)

Contention that one skilled in herbicidal art would have been motivated to use, with acid commonly known as "dicamba," substituted ammonium salt such as that disclosed in two prior references does not warrant holding that claimed substituted ammonium salt of dicamba for use as herbicide is *prima facie* obvious, since there is no suggestion for combining disclosures of those references either in references themselves, which are directed to shampoo additives and production of morpholine, respectively, or in knowledge generally available to those skilled in art.

Case History and Disposition:

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Appeal from the U.S. Patent and Trademark Office, Board of Patent Appeals and Interferences.

Patent application of Rita S. Jones, Michael T. Chirchirillo and Johnny L. Burns, serial no. 07/099,279 (the 2-(2'-aminoethoxy)-ethanol salt of dicamba). From decision upholding rejection of only claim in application, applicants appeal. Reversed.

Attorneys:

Melvyn M. Kassenoff, East Hanover, N.J. (Gerald D. Sharkin and Richard E. Villa, East Hanover; Joanne M. Giesser, Palo Alto, Calif., with him on brief), for appellant.

Harris A. Pitlock, associate solicitor (Fred E. McKelvey, solicitor, with him on brief; Richard E. Schafer, of counsel), for appellee.

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Judge:

Before Rich, Archer, and Clevenger, circuit judges.

Opinion Text

Opinion By:

Rich, J.

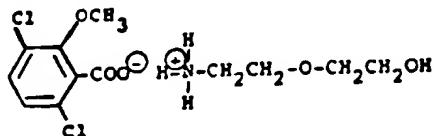
Rita S. Jones et al. (collectively Jones) appeal from the April 15, 1991 decision of the Patent and Trademark Office (PTO) Board of Patent Appeals and Interferences (Board), Appeal No. 90-1920, sustaining the rejection of claim 1, the only claim of application Ser. No. 07/099,279, titled "The 2-(2'-Aminoethoxy) -- Ethanol Salt of Dicamba," as unpatentable under 35 USC 103. We conclude that the PTO has not presented a *prima facie* case of obviousness, and therefore *reverse*.

The Invention

The Claimed invention is a novel salt of 2-methoxy-3, 6-dichlorobenzoic acid, which acid is commonly referred to as "dicamba." A known herbicide, dicamba has typically been sold in the form of its known dimethylamine salt.

The sole claim of the application on appeal reads:

1. The 2-(2'-aminoethoxy) ethanol salt of dicamba.
2. The claimed salt has the following structure:



The Rejection

Claim 1 stands rejected as obvious in view of the combined teachings of the following references:

Richter, U.S. Patent No. 3,013,054, Dec. 12, 1961

Moyle et al., U.S. Patent No. 3,056,669, Oct. 2, 1962

Balassa, U.S. Patent No. 3,725,031, Apr. 3, 1973

Zorayan et al., 88 *Chem. Abstracts* No. 52300j, 1978

Wideman, 86 *Chem. Abstracts* No. 43711a, 1977

Richter, which all agree is the closest prior art, discloses dicamba in free acid, ester, and salt forms, for use as a herbicide. Among the salt forms disclosed are substituted ammonium salts, a

genus which admittedly encompasses the claimed salt. Richter does not specifically disclose the claimed 2-(2'-aminoethoxy) ethanol salt, however. Most notably, Richter discloses (emphasis and bracketed word ours):

Compositions in which X is substituted ammonium are amine salts of 2-methoxy-3, 6-dichlorobenzoic acid [dicamba] and are prepared by the addition of the free acid to various amines. Typical amines which can be used to prepare such amine salts are dimethylamine, trimethylamine, triethylamine, diethanolamine, triethanolamine, isopropylamine, morpholine, and the like. *The resulting products are, respectively, the dimethylamino, trimethylamino, triethylamino, diethanolamino, triethanolamino, isopropylamino, and morpholino salts of 2-methoxy-3, 6-dichlorobenzoic acid.*

Zorayan teaches the amine (H [inf 2] N (CH [inf 2] CH [inf 2] O) [inf 2] H) used to make the claimed salt, as well as the use of that amine in the preparation of surfactants for shampoos, bath preparations, and emulsifiers.

Wideman also teaches the amine disclosed in Zorayan.

The content of the remaining references is unnecessary to our decision.

The Board upheld the examiner's rejection of claim 1 as obvious, finding that the claimed 2-2'-aminoethoxy) ethanol salt of dicamba and the diethanolamine salt of dicamba specifically disclosed by Richter were "closely related in structure," and that based upon the expectation that "compounds similar in structure will have similar properties," a *prima facie* case of obviousness had arisen. The Board found that Jones' rebuttal evidence (Rule 132 declarations and data reported in the specification) failed to "compare the claimed subject matter with the closest prior art," and accordingly did not serve to rebut the *prima facie* case. This appeal followed.

Analysis

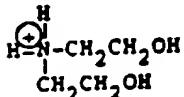
The Solicitor contends that the claimed salt falls within the genus of substituted amine salts of dicamba disclosed by Richter, and that, like Richter's genus, the claimed compound has herbicidal activity. Thus, the Solicitor urges, under the circumstances of this case, (1) the genus/species relationship and (2) the common utility of the claimed and prior art compounds support the Board's holding of *prima facie* obviousness. Moreover, the Solicitor adds, although the claimed compound is neither a homolog nor a position isomer of those salts specifically disclosed in Richter, it is structurally similar thereto, particularly the diethanolamino salt noted by the Board.

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The question of "structural similarity" in chemical patent cases has generated a body of patent law unto itself. 1 Particular types or categories of structural similarity without more have, in past cases, given rise to *prima facie* obviousness; *see, e.g., In re Dillon*, 919 F.2d 688, 692-94, 16 USPQ2d 1897, 1900-02 (Fed. Cir. 1990) (tri-orthoesters and tetra-orthoesters), *cert. denied*,

U.S. ___, 111 S. Ct. 1682 (1991); *In re May*, 574 F.2d 1082, 197 USPQ 601 (CCPA 1978) (stereoisomers); *In re Wilder*, 563 F.2d 457, 195 USPQ 426 (CCPA 1977) (adjacent homologs and structural isomers); *In re Hoch*, 428 F.2d 1341, 166 USPQ 406 (CCPA 1970) (acid and ethyl ester). However, none of these types of structural similarity are involved here. And in any event, this court has previously stated that generalization is to be avoided insofar as specific structures are alleged to be *prima facie* obvious one from the other. *In re Grabiak*, 769 F.2d 729, 731, 226 USPQ 870, 872 (Fed. Cir. 1985).

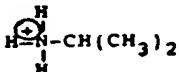
[1] On the basis of the record before us, we cannot sustain the Board's conclusion that the claimed salt and the diethanolamino salt disclosed by Richter are so "closely related in structure" as to render the former *prima facie* obvious in view of the latter. The claimed salt is a primary amine with an ether linkage. The diethanolamino salt disclosed by Richter is a secondary amine, without an ether linkage:



In addition, the only substituted ammonium salt of dicamba expressly disclosed by Richter having an ether linkage is the morpholino salt, which is *cyclic* in structure:



The claimed salt is, plainly, *a* cyclic; i.e., linear. Lastly, while the isopropylamino salt disclosed by Richter is a primary amine, as is the claimed salt, its iso- structure is quite different:



[2] The lack of close similarity of structure is not negated by the fact that the claimed salt is a member of Richter's broadly disclosed genus of substituted ammonium salts of dicamba. The Solicitor contends that " [t]he relative size of the genus disclosed by the prior art would not appear to be a controlling factor in determining whether a *prima facie* case of obviousness exists for a species encompassed within the described genus," citing *Merck & Co. v. Biocraft Labs., Inc.*, 874 F.2d 804, 806-09, 10 USPQ2d 1843, 1845-48 (Fed. Cir.), cert. denied, ___ U.S. ___, 110 S. Ct. 498 (1989). We decline to extract from *Merck* the rule that the Solicitor appears to suggest -- that regardless of how broad, a disclosure of a chemical genus renders obvious any species that happens to fall within it. In *Merck*, at issue on appeal was whether claims to a composition of two diuretics, amiloride and hydrochlorothiazide, present in a particular "medically synergistic" weight ratio, would have been obvious in view of a specific prior art disclosure of amiloride in combination with hydrochlorothiazide, one of 1200 such combinations disclosed in the prior art reference. *Id.* at 806, 10 USPQ2d at 1845. Based on the facts before it, including evidence at trial that the experimentation needed to arrive at the claimed dosage was "nothing more than routine," *Id.* at 809, 10 USPQ2d at 1847, the court affirmed the trial court's determination of obviousness. In contrast, though Richter discloses the potentially infinite genus of "substituted ammonium salts" of dicamba, and lists several such

salts, the salt claimed here is not specifically disclosed. Nor, as we have explained above, is the claimed salt sufficiently similar in structure to those specifically disclosed in Richter as to render it *prima facie* obvious. Every case, particularly those raising the issue of obviousness under section 103, must necessarily be decided upon its own facts.

[3] The Solicitor points out that, given the breadth of forms of dicamba (free acid, ester, or salt) disclosed by Richter as having herbicidal utility, one of ordinary skill in the art would appreciate that the dicamba group has significance with respect to imparting herbicidal activity to dicamba compounds. Thus, the Solicitor contends, one skilled in the art would have been motivated to use, with dicamba, substituted ammonium salts made from a known amine, such as the amine disclosed by Zorayan and Wideman, and would have expected such a salt to have herbicidal activity. Before the PTO may combine the disclosures of two or more prior art references in order to establish *prima facie* obviousness, there must be some sug

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gestion for doing so, found either in the references themselves or in the knowledge generally available to one of ordinary skill in the art. *In re Fine*, 837 F.2d 1071, 1074, 5 USPQ2d 1596, 1598-99 (Fed. Cir. 1988). We see no such suggestion in Zorayan, which is directed to shampoo additives, nor in Wideman, which teaches that the amine used to make the claimed compound is a byproduct of the production of morpholine. Nor does the broad disclosure of Richter fill the gap, for the reasons discussed above.

Conspicuously missing from this record is any *evidence*, other than the PTO's speculation (if it be called evidence) that one of ordinary skill in the herbicidal art would have been motivated to make the modifications of the prior art salts necessary to arrive at the claimed 2-(2'-aminoethoxy) ethanol salt. See *Grabiak*, 769 F.2d at 731-32, 226 USPQ at 872 ("[I]n the case before us there must be adequate support in the prior art for the [prior art] ester/ [claimed] thioester change in structure, in order to complete the PTO's *prima facie* case and shift the burden of going forward to the applicant."); *In re Lalu*, 747 F.2d 703, 705, 223 USPQ 1257, 1258 (Fed. Cir. 1984) ("The prior art must provide one of ordinary skill in the art the motivation to make the proposed molecular modifications needed to arrive at the claimed compound.")

Conclusion

We conclude that the PTO did not establish a *prima facie* case of obviousness, and thus did not shift to Jones the burden of coming forward with unexpected results or other objective evidence of non-obviousness. Accordingly, the decision of the Board is

REVERSED.

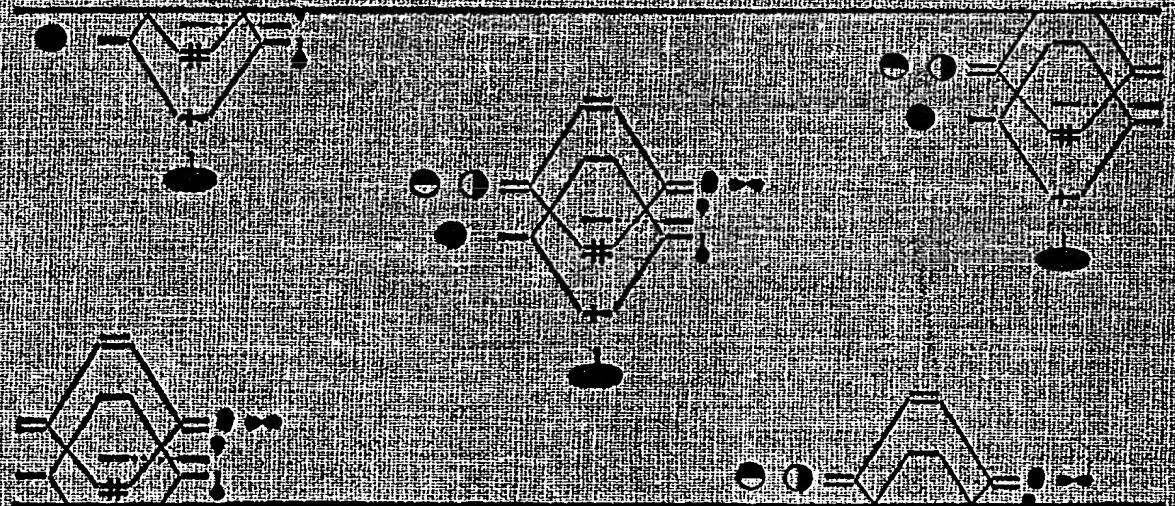
Footnotes

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Footnote 1. *See generally* Helmuth A. Wegner, "Prima Facie Obviousness of Chemical Compounds," 6 *Am. Pat. L. Assoc. O. J.* 271 (1978).

- End of Case -

AB INITIO MOLECULAR ORBITAL THEORY



Warren J. Hehre
Leo Radom
Paul V.R. Schleyer
John A. Pople

AB INITIO MOLECULAR ORBITAL THEORY

WARREN J. HEHRE

University of California, Irvine

LEO RADOM

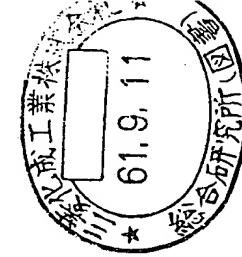
Australian National University, Canberra

PAUL v.R. SCHLEYER

Universität Erlangen-Nürnberg, Erlangen, West Germany

JOHN A. POPPE

Carnegie-Mellon University, Pittsburgh



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atic comparison with experimental data. This aims to educate readers so that they can attach some level of confidence to computational results. Finally, Chapter 7 is an account of recent progress in some fields of chemistry where theory is making major contributions. The examples used are necessarily limited in scope and reflect particular interests of the authors but they should provide a reasonable overview of the current power of *ab initio* theory.

Certain omissions may be noted. No account is given of semiempirical, parameterized methods which parallel *ab initio* theories to some extent. Neither have we attempted to describe some recent more advanced quantum-mechanical methods such as multiconfigurational self-consistent-field theories. The emphasis is on those *ab initio* techniques which are well documented, easy to use, and readily available.

WARREN J. HEHRE

LEO RADOM

PAUL V.R. SCHLEYER

JOHN A. POPLE

Irvine, California
Canberra, Australia
Erlangen, West Germany
Pittsburgh, Pennsylvania
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W.J.H.
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PROLOGUE

The more progress physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of centre to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation [1].

Adolphe Quételet 1796-1874

This book helps to document the extent to which chemistry may now "be submitted to calculation."

The key to theoretical chemistry is molecular quantum mechanics. This is the science relating molecular properties to the motion and interactions of electrons and nuclei. Soon after its formulation in 1925 [2], it became clear that solution of the Schrödinger differential equation could, in principle, lead to direct quantitative prediction of most, if not all, chemical phenomena using only the values of a small number of physical constants (Planck's constant, the velocity of light, and the masses and charges of electrons and nuclei). Such a procedure constitutes an *ab initio* approach to chemistry, independent of any experiment other than determination of these constants. It was also early recognized that solution of the Schrödinger equation was a formidable if not completely impossible mathematical problem for all but the very simplest of systems.

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to solutions which are too complicated to be soluble [3].

P.A.M. Dirac 1902-1984

In practice, the Schrödinger equation has to be replaced by approximate mathematical models for which the possibility of solution exists. The advent of powerful digital computers and of increasingly efficient computer programs has led to significant progress in recent years, both in the development of ever more sophisticated approximate quantum mechanical models and in the application of these models to problems of chemical significance. It is fair to say that theory has now advanced sufficiently far as to provide the chemist with an alternative independent approach to his subject.

It is unlikely that chemistry will change overnight from an experimental to a theoretical science. Much of what now forms its basis may not be subjected to calculation, at least not at present. Nevertheless, it is reasonable to anticipate that an increasing number of chemical investigations which might previously have been performed experimentally will instead be carried out on a digital computer. A number of factors will be responsible for this change in strategy. In many respects theoretical calculations already are more powerful than experiment. They are not bound by practical considerations. Any chemical species may be scrutinized theoretically; calculations on cations, anions, and other reactive intermediates, which might be difficult to investigate experimentally, pose, in principle, no greater problem than calculations carried out on more stable and easily observed molecules. Detailed information about reaction transition structures, excited states, as well as on hypothetical molecular arrangements, deformed molecules, for example, may only be obtained by computation. Calculations are easy to perform and involve little human time and effort relative to the large amount of information obtained. They are becoming less and less costly, whereas experimental work is ever more expensive. Minicomputers, available at a price less than that of a double-focusing mass spectrometer or a research nuclear magnetic resonance instrument, are capable of performing all the calculations described in this book. Expense may well be the decisive factor in determining how investigations are to be carried out in the future.

The quantification of chemistry may not be welcomed by all. Thus,

Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry—an aberration which is happily almost impossible—it would occasion a rapid and widespread degeneration of that science [4].

A. Compte 1798-1857

Even today many chemists are uncomfortable with the thought of using a digital computer as an investigative tool. Many are skeptical. Some are uninformed or even prejudiced. They do not believe that theory is capable of making accurate predictions of chemical phenomena. Some may feel that the theoretical methods are too difficult to learn, let alone apply. One of the primary goals of this book is to help overcome these reservations, and show the extent to which theoretical calculations, in their present stage of development, can be employed as a practical means of doing chemistry.

Although theory will continue to help understand in more detail systems that

have already been investigated experimentally, an exciting prospect is the exploration of new areas of chemistry. Such areas are remarkably large; the vast majority of chemistry remains to be discovered if one considers the whole of the periodic table! Computational work enables the investigator to scrutinize quickly large numbers of seemingly reasonable molecules about which little or nothing may be known. Calculations can help to indicate whether such species are of sufficient interest to justify their preparation and examination, and whether they will be sufficiently stable to make experimental investigation practical. In many instances, the information available theoretically may suffice to answer questions of interest; there may be no need to carry out confirmatory experimental studies. This book describes some of the progress made by theory in "discovering" new chemistry.

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INTRODUCTION

1.1. THEORETICAL MODELS

Two broadly different conceptual approaches to the approximate solution of the Schrödinger equation are possible. In the first, each problem is examined at the highest level of theory currently feasible for a system of its size. Very small systems, such as the helium atom or the hydrogen molecule, can clearly be handled at much higher levels of precision than are feasible for systems containing, say, a hundred or more electrons. In the second approach, with which this book is primarily concerned, a level of theory is first clearly defined after which it is applied *uniformly* to molecular systems of *all* sizes up to a maximum determined by available computational resources. Such a theory, if prescribed uniquely for any configuration of nuclei and any number of electrons, may be termed a *theoretical model*, within which all structures, energies, and other physical properties can be explored once the mathematical procedure has been implemented through a computer program. A *theoretical-model chemistry* results. The model may be *tested* by *systematic* comparison of its findings with known experimental results. If comparisons prove favorable, the model acquires some predictive value in situations where experimental data are unavailable. A number of theoretical models are described in this book, and their range of applicability, their successes, and their failures are thoroughly documented.

A theoretical model should possess a number of important characteristics. First, it should be both *unique* and *well defined*. The procedure for obtaining an energy and a wavefunction as an approximate solution of the Schrödinger equation should

be completely specified in terms of nuclear positions and the number and spins of the electrons in the molecule. A second desirable feature is *continuity*: all *potential surfaces* should be continuous with respect to nuclear displacements. Special procedures must not be used for symmetrical molecules which might lead to results which are discontinuous with those for structures in which the nuclei are slightly displaced to nonsymmetrical positions. A theoretical model should also be *unbiased*. No appeal to "chemical intuition" should be made in setting up the details of the calculation. For example, while calculations in which electrons are assigned to certain "bond orbitals" might be satisfactory for many molecules, they are not suitable for those nuclear configurations where the locations of "bonds" are apt to be ambiguous. A theory can only be used for the analysis of such concepts as bonding if prepositions have not been built into its formulation.

Another important requirement for a satisfactory theoretical model is *size-consistency*: relative errors involved in a calculation should increase more or less in proportion to the size of the molecule. This is particularly important if the model is to be used in a comparative manner, relating properties of molecules of different sizes. While it is generally not possible to satisfy this condition fully, it is often possible to construct models that are *size-consistent for infinitely separated systems*. This means that application of the model to a system of several molecules at infinite separation will yield properties that equal the sum of these same properties for the individual molecules.

It is also desirable that a theoretical model be *variational*, that is, yield a total energy that is an *upper bound* to that which would result from exact solution of the full Schrödinger equation.

Finally, a practical theoretical model should be capable of implementation on a computer and be usable with minimal human and computational effort. This enables application of the model to extensive exploration of the properties of a large number of molecules. The development of efficient programs for such models is a major area of research in present-day theoretical chemistry.

1.2. MOLECULAR ORBITAL MODELS

The theoretical models discussed in this book are all based on *molecular orbital (MO) theory*. This approximate treatment of electron distribution and motion assigns individual electrons to one-electron functions termed *spin orbitals*. These comprise a product of spatial functions, termed *molecular orbitals*, $\psi_1(x, y, z)$, $\psi_2(x, y, z)$, $\psi_3(x, y, z)$, \dots , and either α or β *spin components*. The spin orbitals are allowed complete freedom to spread throughout the molecule, their exact form being determined variationally to minimize the total energy. In the simplest version of the theory, single assignment of electrons to orbitals (sometimes called an *electron configuration*) is made. These orbitals are then brought together to form a suitable *many-electron wavefunction* Ψ which is the simplest MO approximation to the solution of the Schrödinger equation.

In practical calculations, the molecular orbitals ψ_1, ψ_2, \dots are further restricted

to be linear combinations of a set of N known one-electron functions $\phi_1(x, y, z)$, $\phi_2(x, y, z)$, \dots , $\phi_N(x, y, z)$:

$$(1.1) \quad \psi_i = \sum_{\mu=1}^N c_{i\mu} \phi_{\mu}.$$

The functions $\phi_1, \phi_2, \dots, \phi_N$ (which are defined in the specification of the model) are known as *one-electron basis functions*, or simply as *basis functions*. They constitute the *basis set*. If the basis functions are the *atomic orbitals* for the atoms making up the molecule, Eq. (1.1) is often described as the *linear combination of atomic orbitals (LCAO) approximation*, and is frequently used in qualitative descriptions of electronic structure.

Given the basis set, the unknown coefficients $c_{i\mu}$ are determined so that the total electronic energy calculated from the many-electron wavefunction is minimized and, according to the *variational theorem*, is as close as possible to the energy corresponding to exact solution of the Schrödinger equation. This energy and the corresponding wavefunction represent the best that can be obtained within the *Hartree-Fock approximation*, that is, the best given the constraints imposed by: (a) the use of a limited basis set in the orbital expansion, and (b) the use of a single assignment of electrons to orbitals.

Hartree-Fock models are the simplest to use for chemical applications and have been employed in many of the studies carried out to date. To specify the model in full, it is only necessary to define a unique basis set $\phi_1, \phi_2, \dots, \phi_N$ for any nuclear configuration. This is conveniently done by having a standard set of basis functions for each nucleus, centered at the nuclear position, which depend only on the corresponding atomic number. Thus, there would be a set of functions for each hydrogen atom and other sets for each carbon and so forth. In the simplest Hartree-Fock models, the number of basis functions on each atom will be as small as possible, that is, only large enough to accommodate all the electrons and still maintain spherical symmetry. As a consequence, the molecular orbitals (1.1) will have only limited flexibility. If larger basis sets are used, the number of adjustable coefficients in the variational procedure increases, and an improved description of the molecular orbitals is obtained. Very large basis sets will result in nearly complete flexibility. The limit of such an approach, termed the *Hartree-Fock limit*, represents the best that can be done with a single electron configuration. As is shown in later chapters, theoretical-model chemistry at the Hartree-Fock limit has become fairly well characterized, and many of its successes and limitations are now well documented.

The main deficiency of Hartree-Fock theory is its incomplete description of the *correlation* between motions of the electrons. Even with a large and completely flexible basis set, the full solution of the Schrödinger equation cannot be expressed in terms of a *single electron configuration*, that is, a unique assignment of electrons to orbitals. To correct for such a deficiency, it is necessary to use wavefunctions that go beyond the Hartree-Fock level, that is, that represent more than a single electron configuration. If Ψ_0 is the full Hartree-Fock many-electron wavefunction,

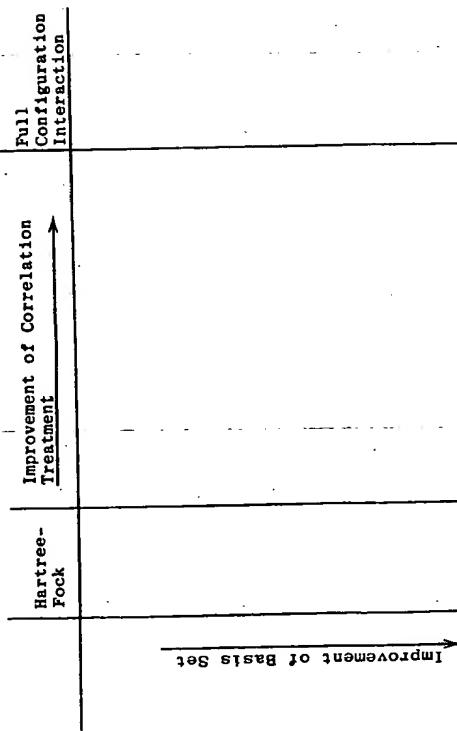


FIGURE 1.1. Schematic representation of theoretical models showing basis set improvement vertically and correlation improvement horizontally.

the extended approximate form for the more accurate wavefunction Ψ is

$$\Psi = a_0 \Psi_0 + a_1 \Psi_1 + a_2 \Psi_2 + \dots \quad (1.2)$$

Here Ψ_1, Ψ_2, \dots are wavefunctions for other configurations, and the linear coefficients a_0, a_1, \dots are to be determined. Inclusion of wavefunctions for all possible alternative electron configurations (within the framework of a given basis set) is termed *full configuration interaction*. It represents the best that can be done using that basis set. Practical methods, which may be sequenced in order of increasing sophistication and accuracy, seek either to limit the number of configurations or to approximate the effect which their inclusion has on the total wavefunction.

The two directions in which theoretical models may be improved can be shown with a two-dimensional chart as in Figure 1.1. The simplest type of model is a Hartree-Fock treatment using a small basis set. This would be placed at the top left of the diagram. As more sophisticated models are applied, an investigation may move downwards (improvement of the basis set) or from left to right (improvement of correlation technique). The bottom row, which may not be realizable in practice, represents various methods using a completely flexible basis. The right-hand column, which may also be impractical, represents full configuration interaction with a given basis. The bottom right-hand corner corresponds to full configuration interac-

tion with a completely flexible basis set. Notice that the two directions on this chart correspond precisely to the two approximations which have been made in order to replace the full Schrödinger equation by practical molecular orbital schemes capable of application to diverse systems. Progression in the vertical direction ("Improvement of Basis Set") corresponds to increasing flexibility of the one-electron spin orbitals [Eq. (1.1)]. Progression in the horizontal direction ("Improvement of Correlation Treatment") corresponds to improved flexibility arising from taking the sum of an increasing number of many-electron functions [Eq. (1.2)]. It follows, therefore, that the bottom right-hand corner of the diagram constitutes the exact solution of the nonrelativistic Schrödinger equation.

The main objective of this book is to describe and to document the performance of a number of theoretical models which comprise such an investigational chart. Many of the applications to date have been at the Hartree-Fock level (left-hand column in Figure 1.1); this is reflected in the coverage of subsequent chapters. However, sufficient investigations have now been carried out beyond Hartree-Fock to enable some assessment of the performance of such theoretical models.